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Homo- and Copolymerization of
(Methacryloylethenedioxy)pentachlorocyclotriphosphazene

by

Douglas E. Brown and Christopher W. Allen

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University of Vermont
Department of Chemistry
Burlington, VT 05405-0125

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Homo- and Copolymerization of (Methacryloyl ethenedioxy)-pentachlorocyclotriphosphazene.

Douglas E. Brown and Christopher W. Allen*,
Department of Chemistry, University of Vermont,
Burlington, VT 05405-0125

Abstract

A new organofunctional cyclophosphazene monomer, (Methacryloyl ethylenedioxy)pentachlorocyclotriphosphazene ($\text{N}_3\text{P}_3\text{Cl}_5\text{OCH}_2\text{CH}_2\text{OC}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2$, **I**) has been prepared from 2-hydroxyethylmethacrylate and hexachlorocyclotriphosphazene. Radical initiated homopolymerization of **I** and copolymerization of **I** with methylmethacrylate proceeds readily. The new flame retardant polymers have been characterized by elemental analysis, NMR spectroscopy, gel permeation chromatography, membrane osmometry and TGA. Reactivity ratios and Alfrey-Price parameters for the methylmethacrylate copolymerization show a significant effect of the phosphazene on the olefin reactivity.

Introduction

Work in our laboratories has resulted in the development of hybrid inorganic-organic phosphazene polymers which contain cyclophosphazenes as substituents on carbon chains [1]. These materials are in contrast to the well established poly(phosphazenes) in which the backbone is a linear phosphazene unit [2]. While our earlier investigations focused on copolymers of alkenylfluorocyclotriphosphazenes [3-5] and organic comonomers, recent investigations have focused derivatives of the more readily available hexachlorocyclotriphosphazene, $\text{N}_3\text{P}_3\text{Cl}_6$. Vinyloxychlorocyclotriphosphazenes undergo radically induced homopolymerization to yield high molecular weight linear polymers [1,6,7] similarly, Inoue has shown that 4'-vinyl-4-biphenyloxy-pentahalocyclotriphosphazenes are excellent monomers for addition polymerization [8,9] as are the products of the reactions of vinyl containing aldehydes with phosphazene anions which have been prepared and polymerized by van de

Grampel[10].

The next step in our investigations is to develop cyclophosphazene monomers derived from (relatively) inexpensive starting materials and which can be copolymerized with standard organic monomers thus allowing for incorporation of useful cyclophosphazene properties into traditional polymers. One organic substrate suitable for incorporation into cyclophosphazenes is 2-hydroxyethylmethacrylate. The reaction of excess 2-hydroxyethylmethacrylate with $N_3P_3Cl_6$ has been shown to yield hexa(methacryloyl ethenedioxy)cyclotriphosphazene, $N_3P_3[COH_2CH_2OC(CH_3)=CH_2]_6$, which readily forms a cross-linked matrix suitable for dental resins [11,12]. In addition to low cost and facile polymerization, this (methacryloyl ethenedioxy) functionality is particularly attractive due to the fact that the olefinic center might be expected to be electronically isolated from the cyclophosphazene. This separation would avoid certain of the complications previously observed when the olefin is subjected to electronic perturbation by the phosphazene. In this paper we report the preparation of (methacryloylethenedioxy)pentachlorocyclotriphosphazene along with homopolymerization and methylmethacrylate copolymerization reactions.

Experimental Section

Materials. Benzene[13] was distilled from potassium under nitrogen prior to use. Methylmethacrylate was distilled from calcium hydride under nitrogen and stored at -20° . Azobisisobutyronitrile (AIBN) was recrystallized three times from methanol, vacuum dried and stored at -20° under nitrogen. Hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, (Nippon Soda), hydroxyethylmethacrylate, HEMA, and anhydrous pyridine (Aldrich) were used without further purification

Measurements. NMR spectra were recorded on a Bruker WM250 spectrometer

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with an Aspect 3000 computer. Operating frequencies were 250.1 MHz (^1H), 62.9 MHz (^{13}C), and 101.12 MHz (^{31}P). Tetramethylsilane (^1H and ^{13}C) was used as an internal reference and 85% H_3PO_4 (^{31}P) was used as an external reference. Chemical shifts upfield from the reference were given a negative sign. Broad band ^1H decoupling was used for ^{13}C and ^{31}P spectra. Infrared spectra were obtained as thin films on NaCl disks or as KBr disks using a Perkin Elmer 1430 spectrophotometer. Polymer films were cast from dichloromethane solutions. Mass spectra were recorded on a Finnigan 4610 spectrometer operating at 80eV. Gel permeation chromatography was performed on a Waters 6000A high performance liquid chromatograph equipped with Waters 10 μ A and 10 μ A microstyragel columns. Membrane osmometry was done using a Wescan Medel 230 recording membrane osmometer. Thermal analysis was performed on a Perkin Elmer Thermal Analysis Data Station interfaced with a TGS-2 Thermogravimetric System, a DSC-4 Differential Scanning Calorimeter, and a DTA Differential Thermal Analysis System. Elemental analysis was performed by Robertson Laboratory, Inc. Copolymer polymer composition was determined from weight percent nitrogen [3]. Reactivity ratios for the terminal model were calculated using the Mortimer-Tidwell non-linear least square approach [14] and for the penultimate model by the methodology developed by Pittman [15] was employed.

Preparation of (methacryloyl ethylenedioxy)pentachlorocyclotriphosphazene, $\text{N}_3\text{P}_3\text{Cl}_5(\text{OCH}_2\text{CH}_2\text{O}(\text{C}=\text{O})\text{C}(\text{CH}_3)=\text{CH}_2)$ (1). A 250ml round bottom flask was charged with 15.00 g (0.043 moles) of $\text{N}_3\text{P}_3\text{Cl}_6$, and equipped with a magnetic stirrer, reflux condenser, and a septum. The apparatus was then evacuated and backfilled with nitrogen using a Schlenk line, and kept under nitrogen pressure. A syringe was used to introduce 50 ml of dry benzene into the flask and the stirrer started. After the

phosphazene had dissolved, 6 ml (0.046 moles) of HEMA and 5ml (0.062 moles) of dry pyridine were introduced into the vessel by syringe. The solution was then heated to 40°C for 48 hours. After allowing the reaction to cool to room temperature, 50 ml of benzene were added and the solution was filtered and washed successively with 2M HCl (twice), 2M K₂CO₃, then a saturated NaCl solution. The organic layer was dried over anhydrous MgSO₄, filtered, and the most of the benzene was removed by rotary evaporation using a water bath at 35°C to give 28 g of solution. The resulting crude product was stored at -20°C, and was stable for several weeks at this temperature. Immediately prior to use, the solution was allowed to melt, and 8.20g of the solution purified by flash chromatography, using a solvent mixture of 8% diethyl ether in low boiling petroleum ether. The middle two thirds of the fractions containing the product were then added to a 500 ml round bottom flask and the solvent was removed by rotary evaporation using a water bath at 35°C. The resulting clear, viscous liquid was subjected to three freeze, pump, thaw cycles to give 1.70 g (30.5% of theory) of the product (I).

Samples of pure I rapidly undergo polymerization at elevated temperature and hence bulk purification by distillation is not feasible. Short path distillation at reduced pressure (0.005 mmHg) of a sample containing anhydrous CuSO₄ as a (polymerization inhibitor) yielded a small sample of pure material. The pure material slowly undergoes both rearrangement and polymerization reactions and thus was not submitted for elemental analysis. The identity of I was unambiguously established by standard analytical methods. Calc. for N₃P₃Cl₅[OCH₂CH₂OC(O)C(CH₃)=CH₂]: Mol. wt. 439. Found mol. wt 439 (mass spectrum, Cl, 439).

¹H NMR[16] δ_{H_a} 5.6(1H), ²J_{H_aH_b} = 1.5; δ_{H_b} 6.18 (1H); δ_{H_{CH₂}} 4.40-4.44 (4H); δ_{CH₃} 1.96 (3H). ¹³CNMR[16] δ₁ 62.3, ²J_{PC}=9.5; δ₂ 67.0, ³J_{PC}=7.5; δ₃ 167.0; δ₄ 136.0; δ₅ 18.2; δ₆

126.4. ^{31}P NMR: δ_{PCl_2} 23.6, $^3J_{\text{PP}}=63.7$; $\delta_{\text{PCl(OR)}}$ 16.4. IR: 2958 (m, ν_{CH}), 1723 (s, $\nu_{\text{C=O}}$), 1636(m, $\nu_{\text{C=C}}$), 1220 (s, ν_{PN}), 1170(s, ν_{CO}), 1118(w, ν_{PO}) 1072, 1034 (s, ν_{PO}), 872 (m, PN), 748(m, PCl).

Preparation of poly(methacryloyl ethylenedioxy)pentachloro-

cyclotriphosphazene, $[\text{N}_3\text{P}_3\text{Cl}_5\text{OCH}_2\text{CH}_2\text{OC(O)C(CH}_3\text{)CH}_2]_n$. Immediately after isolation, a sample of **I** was weighed into 12cm thick walled glass tubes with 24/40 outer joints at the top, 1-2% (by weight) of AIBN was added and then diluted 50% with dry benzene. A vacuum adapter was fitted to the tops of the vessel and connected to a Schlenk line. The sample was then subjected to three freeze, pump, thaw cycles, backfilled with nitrogen, sealed and placed in a bath at $60 \pm 2^\circ\text{C}$. The polymerization was allowed to proceed until the sample was a very viscous liquid that would still flow. This condition was typically reached at 10-20% conversion of monomer to polymer. At this point the polymerization was terminated by adding approximately 25 ml of CH_2Cl_2 and dissolving the polymer. The polymer was then precipitated by slowly adding the polymer solution to a large excess of methanol. The precipitated polymer was allowed to settle to the bottom of the beaker, overnight if necessary, the excess solvent decanted off, and the polymer filtered, washed, and vacuum dried. Anal. Calcd for $[\text{N}_3\text{P}_3\text{Cl}_5\text{C}_8\text{H}_9\text{O}_3]_n$: C, 16.33; H, 2.04; N, 9.52. Found: C, 18.51; H, 2.34; N, 9.52. Molecular weight data may be found in Table I.

Bulk polymerization of **I** leads to a sticky, insoluble and presumably crosslinked material.

Preparation of poly[(methacryloyl ethylenedioxy)-pentachlorocyclotriphosphazene-co-methylmethacrylate],

$[(\text{N}_3\text{P}_3\text{Cl}_5\text{OCH}_2\text{CH}_2\text{OC(O)C(CH}_3\text{)CH}_2)_x(\text{CH}_3\text{OC(O)C(CH}_3\text{)CH}_2)_y]_n$. Copolymerizations

using various mole fraction of **I** and methylmethacrylate were conducted in a fashion identical to the homopolymerization experiments described above. Copolymer composition was determined by the amount of nitrogen as determined by elemental analysis. Molecular weight data may be found in Table **I** and copolymer composition in Table **II**.

Results and Discussion

The reaction of HEMA and $N_3P_3Cl_6$ in the presence of pyridine leads to the new organofunctional phosphazene monomer $N_3P_3Cl_5O(CH_2)_2OC(O)C(CH_3)=CH_2$ (**I**) along with the easily separable $N_3P_3Cl_6$. Special care is required in handling **I** due to its propensity to undergo thermal polymerization and ambient temperature rearrangement. The rearrangement process will be the subject of a future communication. The identity of **I** has been established by the use of standard characterizational techniques. The mass spectrum (C.I.) shows the molecular ion and significant amounts of the $C_2H_4OC(O)C(CH_3)=CH_2$ (M/e 113) fragment. The ir spectrum shows the PN and methacrylate (e.g. $\nu C=O$, $\nu C=C$) function along with a strong PO stretching frequency. The 1H NMR spectrum shows methyl, methylene and vinyl resonances. The ^{13}C NMR spectrum confirms the presence of the carbonyl and vinyl groups and shows phosphorus coupling to the methylene carbon atoms. The AX_2 ^{31}P NMR spectrum is typical of a monosubstituted derivative[17] with shifts appropriate for $\equiv PCl_2$ and $\equiv PCl(OR)$ centers. The preparation and polymerization reactions of **I** are summarized in Scheme 1.

Insert Scheme 1

The poly(methacryloylphosphazene) formed from bulk polymerizations of **I** using AIBN as an initiator was sticky and insoluble, indicating a crosslinked material. Soluble polymers could be formed by polymerization in benzene [13] solution. The resulting

polymer was soluble in non-and moderately polar solvent but insoluble in hydroxylic solvents. Solution copolymerization of **I** with methylmethacrylate (MMA) proceeds readily to give copolymers with a wide range of composition (Table **II**).

Given our previous observation of significant penultimate effects in the copolymerization of phosphazene derivatives of α -methylstyrene with methylmethacrylate[5], we calculated reactivity ratios using the terminal and penultimate models (Table **III**). The penultimate reactivity ratio program is very sensitive to small changes in copolymer composition. Therefore, significant differences between r_1 and r_1' and/or r_2 and r_2' for a copolymer system would have to be calculated to confirm penultimate effects. The copolymer composition data of this experiment, determined by nitrogen microanalysis, is probably not accurate enough to attribute the differences observed between the r and r' values in this experiment to penultimate effects. However, it can be reasonably concluded that no penultimate effects of any significance exist for this copolymerization. The reactivity ratios from the terminal model should then be accurate. These reactivity ratios show that the methacryloylphosphazene monomer is less reactive in this system than MMA. The Q and e values calculated for the phosphazene monomer from these reactivity ratios and the known Q and e values for MMA are listed with some reference values in Table **IV**. From these results it is apparent that the phosphazene substituent has a significant effect on polarity of the vinyl group. The large positive value of e calculated for the phosphazene monomer versus the negative value of e for HEMA indicates that the phosphazene substituent has a strong electron withdrawing effect on its vinyl group, even though it is several bonds removed. However, based on the wide variety of e values for these monomers as shown in Table **IV**, long range effects do not seem to be unusual for methacrylates. A plot of the 95% confidence limits for the

reactivity ratios shows a lack of excess eccentricity which indicates that the data is self consistent and also consistent with their terminal model of copolymerization.

Based on GPC data (calibrated against polymethylmethacrylate standards), the poly(methacryloylphosphazene) formed a moderate molecular weight homopolymer. However, the \bar{M}_n determined for this polymer by membrane osmometry is significantly higher than the GPC value. This result has been observed to some degree for all the \bar{M}_n values of polymers derived from vinylphosphazenes determined by both methods[3-5]. These contradictory results may be arising from diffusion of low molecular weight chains across the membrane. This would result in inflated \bar{M}_n values. This problem is expected for the poly(methacryloyl phosphazene) based on its low GPC M_n . The fact that the M_n value determined osmotically for a high molecular weight copolymer is comparable to (in fact slightly lower than) the GPC value suggests that the GPC results give a reasonable evaluation of the molecular weights. The molecular weights of the I/MMA copolymers decrease with increasing phosphazene in the feed. The same result has occurred in all the previous copolymerizations between vinylphosphazenes and organic monomers[3-5], and indicates that the phosphazene monomer is acting as a chain transfer or terminating agent. Consequently, reduced molecular weights from the poly(methacryloyl phosphazene) homopolymer may be expected.

The ^{13}C NMR spectrum of the methacryloylphosphazene homopolymer and a copolymer of this monomer with MMA were examined to assess the effects of the phosphazene substituent on the polymer structure. By comparing relative triad intensities of the ^{13}C resonances from the carbonyl carbon atom, the methyl carbon atom, and the quaternary backbone carbon atom of homopolymers with poly(MMA), it is evident that the tacticities of these two polymers are nearly the same. Integration of the resonances from

the methyl group of the phosphazene monomer indicate a rr:mr:mm triad ratio of 0.60:0.39:0.01, very close to the same ratio for poly(MMA) formed with radical initiation[18]. Therefore, the phosphazene substituent of the monomer apparently has little effect on the effect of the vinyl backbone structure. The ^{13}C spectrum of the copolymer is similar to that of the homopolymers, however, what appears to be two overlapping sets of triads appears in the region where the quaternary carbon resonances are expected. The copolymer composition was a 3.6:1 ratio of MMA to phosphazene so the lower intensity, downfield set of triads is then probably from the methacryloylphosphazene comonomer, and the larger set of triads is from the MMA unit.

A TGA scan of the poly(methacryloylphosphazene) indicates that a small weight loss occurs at 210°C followed by another larger weight loss at 300°C. The total weight loss for these two steps is 37% of the original mass, corresponding to the loss of HCl in the first step and loss of HEMA or the rest of the organic material in another form at the second step. Loss of HCl in the first step was confirmed by the observation of HCl as the major fragment in the mass spectrum when the polymer is heated in the mass spectrometer in the general temperature range of the first decomposition step. The remaining mass is lost at 630° with no char remaining.

The flame retardant effect of the phosphazene was examined by exposing a sample to a flame, removing it after ignition and observing the time required to self extinguish. The methacryloylphosphazene/MMA copolymers exhibited different degrees of flame retardency depending on their compositions. The copolymers that were composed of less than 15 mole percent phosphazene showed little improvement in flame retardency over MMA, while those with higher incorporations of the phosphazene monomer would self extinguish in less than one second. The poly(methacryloylphosphazene) self

extinguishes immediately upon removal of the external flame.

In summary, we have developed a new organofunctional chlorophosphazene which can either undergo homopolymerization or copolymerization with organic comonomers. Further studies of this and related chlorophosphazene substituted polymers are in progress.

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Scheme 1

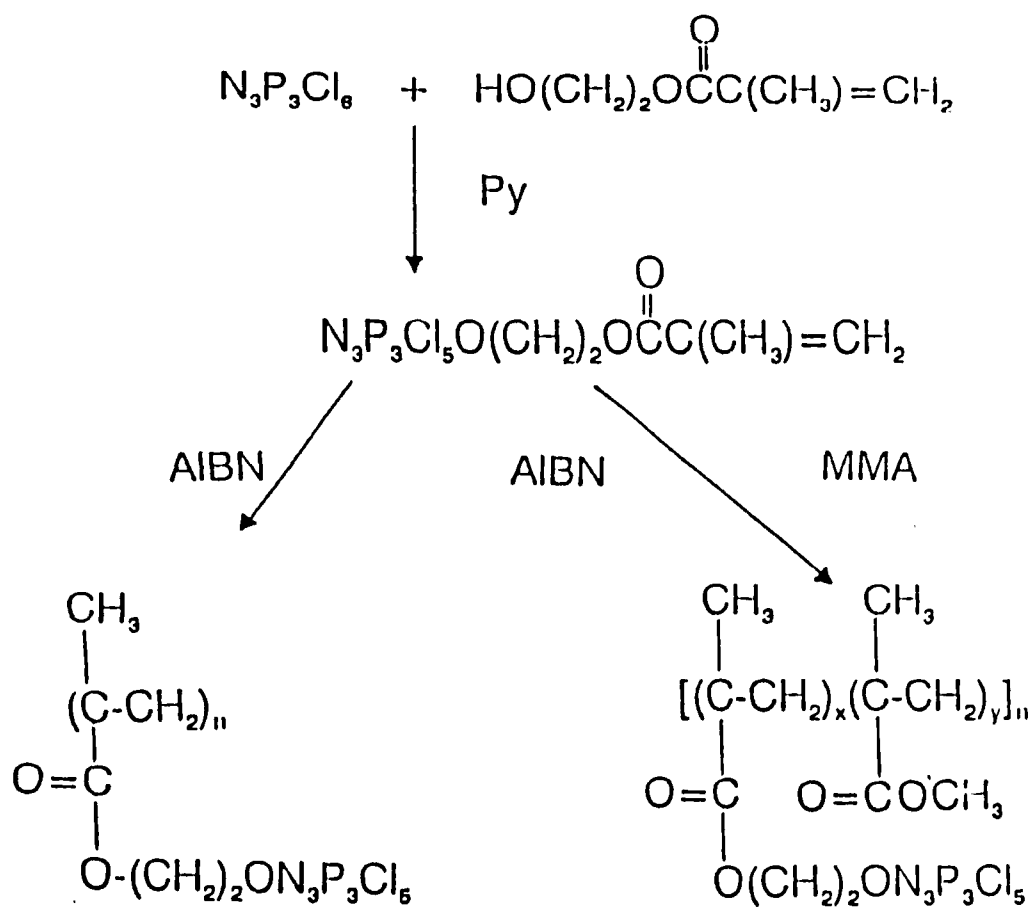


Table I

Selected Molecular Weight Data for (Methacryloyl ethylenedioxy)pentachlorocyclotriphosphazene Homo- and Copolymers.*

<u>Polymer^b</u>	<u>I, mol %</u>	<u>10³\bar{M}_w</u>	<u>10³\bar{M}_n</u>
poly (I)	100%	67.0	55.9
poly (I)	100%		80.7 ^c
poly (I/MMA)	44.1	128.3	89.7
poly (I/MMA)	34.9	137.2	90.5
poly (I/MMA)	23.5	78.5	56.4
poly (I/MMA)	12.6	257.5	132.4
poly (I/MMA)	7.4	318.7	184.1
poly (I/MMA)	7.4		156.0 ^c

a. Molecular weights determined by GPC except where indicated

b. I = $N_3P_3Cl_5O(CH_2)_2OC(O)C(CH_3)=CH_2$; MMA=Methylmethacrylate

c. Determined by membrane osmometry.

Table II

Composition and Conversion Data for (Methacryloyl ethylenedioxy)pentachlorocyclotriphosphazene (I) Methylmethacrylate (MMA) Copolymerizations

Feed	I, Mol %		% Conversion
		Copolymer	
57.72		44.05	25.16
46.34		34.91	32.22
28.02		21.59	26.56
15.57		12.27	20.47
50.27		43.90	25.16
35.78		31.86	14.71
10.33		8.72	13.42
8.57		7.40	14.28
31.65		27.08	22.87
27.21		23.53	26.13
11.38		9.92	20.00
14.40		12.56	17.45
51.39		45.57	14.20
37.36		33.24	17.48

/

Table III

Comparison of Terminal and Selected Pennultimate Reactivity Parameters for the (Methacryloyl ethylenedioxy)pentachlorocyclotriphosphazene (M_2) methymethacrylate (M_1) Copolymerization

Model	r_1	r_1'	r_2	r_2'
Terminal	1.08	-	0.46	-
Pennultimate ^a	1.44	0.64	0 ^b	0.85

a. $r_1 = k_{111}/k_{112}$ $r_1' = k_{211}/k_{212}$. b. Assumed to be 0 from the calculated value of -0.26.

Table IV
Alfrey Price Parameters for Various Methacrylates

Monomer	Q	e
Methacryloylphosphazene ^a	0.96	1.24
MMA ^b	0.74	0.40
HEMA ^b	1.78	-0.39
Methacryloyl chloride ^b	2.04	1.54
Methacrylic acid ^b	0.98	0.62

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